

Impurity effect on low-temperature polarisation of the charge-density-waves in o-TaS₃

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Abstract

The temperature dependence of the low-temperature dielectric response is studied in o-TaS₃ samples doped by Nb, Se, and Ni and for nominally pure ones. It is found, that the low-temperature dielectric constant depends anomalously on doping and is higher for doped crystals, whereas the temperature dependence of the characteristic time of all samples follows the activation law with nearly the same activation energy ~ 400 K ($T > 20$ K). The observed behaviour is inconsistent with all available explanations of the low-temperature dielectric anomaly.

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I. INTRODUCTION

Quasi-one dimensional conductors like TaS_3 , $\text{K}_{0.3}\text{MoO}_3$ *etc.* are well known physical systems which undergo spontaneous structural transition into a low-temperature ordered state, where one of the most widely studied electronic crystal - the charge-density waves (CDWs) - is formed [1]. Similarity between the physical properties of the CDW conductors, Wigner crystals, vortex lattices in superconductors, together with the specific possibility of measurements of extremely small displacements of the electronic crystal, that in the case of the CDW is associated with extremely high dielectric constant ε up to 10^8 , makes the CDW conductors one of the most convenient model system for investigation of the collective response to an external force.

In quasi-one dimensional conductors at an electric field high enough to overcome the CDW-impurity interaction the CDW starts to slide providing a contribution in nonlinear conduction. At relatively small electric fields the CDW is pinned by impurities, and its response to an electric field may provide an information on CDW-impurity interaction, as well as on the CDW state itself. In the recent years the interest to dielectric properties of the CDW conductors have been revived because of observation of the low-temperature anomaly of their $\epsilon(\omega, T)$ for low frequencies $\omega \sim 10^{-2} - 10^5$ Hz [2–6]. The origin of this anomaly remains to be the subject of intensive study and discussion [2–8].

Many experimental facts show that the CDW at sufficiently low temperatures is characterised by "glassy" behaviour (see [9] and references therein) related to the existence of metastable states in the CDW system. In particular, the rough free energy landscape caused by pinning of the CDW leads to a continuous relaxation times spectrum that reveals itself in a long-time logarithmic relaxation of polarisation. In the framework of this "glassy" approach the temperature maximum in $\epsilon(\omega, T)$ marks the critical slowing down of the CDW kinetics, when the system goes through a temperature-dependent characteristic time $\tau(T)$ into a glassy state [2], which in the case of TaS_3 was recognised as a disorder-induced glassy state [5,6].

Alternative explanations of the low-temperature anomaly were given recently [7,8]. On the first hand, Volkov [7] analysed the screening effects on a deformed CDW presented in the form of a periodic chain of phase solitons pinned by impurities. It was shown, that the characteristic time of the dielectric response of such a system follows an activation law. In the framework of this approach the activation energy of $\tau(T)$ corresponds to the activation energy of the linear conduction, in agreement with the experimental data for $\text{K}_{0.3}\text{MoO}_3$ [2–4], $(\text{TaSe}_4)_2\text{I}$ [10] and TaS_3 at $T \sim 100$ K [11,12]. Note that for these materials, as well as for all known CDW materials, the dielectric constant *decreases* with increasing impurity concentration.

On the other hand, Brazovskii and Larkin [8] considered a phenomenological model of pinning, taking into account both local and collective types of pinning. It was shown that the characteristic time of the dielectric response of the pinned CDW follows an activation (in the case of a single pinning energy) or close to activation law (in the case of a distribution of the pinning energy) with the activation energy close to the pinning energy. The dielectric constant also *decreases* with increasing impurity concentration.

So the question on the origin of the low-temperature CDW polarisation anomaly remains to be open. At the same time, there is a way to distinguish experimentally between the explanations given above. For this purpose it is necessary to study the characteristic time, τ , and the dielectric constant, ϵ , as a function of the temperature, impurity concentration, n_i , and their chemical type. If the maximum of the dielectric response is due to the disorder-induced glass transition [5,6], the characteristic time τ increases with increasing impurity concentration n_i . If the maximum is related to the screening mechanism [7], $\tau(T)$ has the same activation energy as the screening carrier concentration (i.e. as the linear conduction). If the maximum is related to the pinning energy, the activation energy depends on a chemical type of dominating doping impurity, but is independent of their concentration. In all cases [2–8] the dielectric constant *decreases* with increase of impurity concentration.

In this paper we present results of the real-time low-temperature polarisation measurements of o-TaS₃ doped by Nb, Ni, and Se, as well as for pure one. The measurements were

carried out over the time interval from $1\ \mu\text{s}$ to $10^3\ \text{s}$ in the temperature range 1.6-32 K. Our results show that the characteristic time follows the activation law with the activation energy independent of the doping element and its concentration, whereas the activation energy of the linear conduction varies within a factor 2. It is also found that the dielectric constant is higher for impure crystals. Our results are therefore inconsistent with all available explanations of the low-temperature dielectric anomaly and indicate that there are subgap excitations of the CDW mediating its low-temperature polarisation.

II. EXPERIMENTAL

A real-time relaxation technique is appropriate to reveal the characteristics of the transport properties of the CDW and the low-frequency CDW excitations [2,13,14]. The time-domain measurements are free from the integral effects inherent to the frequency-domain technique in case of presence of internal interactions in the system [15]. We studied the dielectric response of o-TaS₃ samples that arises during the application of an alternating-sign periodic train of voltage pulses (see inset in Fig. 1). Unlike the earlier measurements on the blue bronzes [2,13] the polarisation charge Q was measured as a function of time t after switching the polarisation voltage across the sample, V , to its *zero* value. The $Q(t)$ curves were averaged over a large number of pulses (order of 100). Such zero voltage measurements allows us to get rid of the ohmic contribution of thermally activated quasi-particles, that is essential at long times and high temperatures. For the measurements we have used a hand-made integrator on the base of LMC6001 ultra-low input current amplifier. The low-frequency noise of the apparatus is of the order of $3 \times 10^{-16}\ \text{A}/\sqrt{Hz}$ (at 1 kHz).

In addition, to compare the time-domain technique with frequency-domain technique we undertook measurements of real and imaginary parts of AC conduction in a frequency range 10 Hz - 10 kHz with using SR530 lock-in amplifier as a phase-sensitive detector.

o-Ta₃ crystals as well as bundles originating from two different sources were investigated. Three batches were prepared at the Switzerland University and was kindly supplied to us by

TABLE I.

Sample	Nominal Impurity Content	T_p K	E_T V/cm	E_σ K	E_ϵ K	$\epsilon(0.1 \text{ s})^\dagger$ $T = 20 \text{ K}$	$\sigma''(1 \text{ kHz}, 10 \text{ K})/\sigma(100 \text{ K})$
1 ^{a,b}	pure	221	0.4	400	420	1.33×10^6	3.9×10^{-5}
2 ^{a,b}	pure	221	0.4		456	1.76×10^6	
3 ^c	pure	220	1.4	360	437	3.43×10^6	1.8×10^{-5}
4 ^c	0.2%Nb	205	> 35	370	440	3.31×10^6	1.5×10^{-4}
5 ^c	0.5%Nb	202	> 20		476	7.15×10^7	6.1×10^{-4}
6 ^b	5%Ni	219	‡	370	395	1.14×10^7	9.9×10^{-5}
7 ^b	1%Se	212	5	260	446	1.81×10^7	1.9×10^{-4}

^aSamples from the same batch.

^bSamples prepared in IRE RAS (Moscow, Russia).

^cSamples prepared in the Institut de Physique Appliquee (Lausanne, Switzerland).

†The dielectric constant was calculated as $\epsilon(t) = (1/\epsilon_0)[Q(t)/V](L/S)$ where L is the length and s is the cross-sectional area of a sample.

‡I-V curves are nonlinear and have no threshold.

Dr. F. Levy. Other ones were prepared by us in IRE RAS (Moscow, Russia). The contacts to the samples were cold soldered 50- μm In wires. The samples characteristics are briefly summarised in Table I.

III. RESULTS

First of all we got sets of polarisation charge *vs.* polarisation pulse amplitude dependencies to find the linear response region. A voltage corresponding to this region for all temperatures was chosen for further detailed study of the response over entire temperature range. The results presented below corresponds to the linear response region.

The curves obtained at a fixed polarisation pulse duration t_p are well reproducible. Comparing the $Q(t)$ curves measured for various t_p we have detected a weak dependence of $Q(t)$

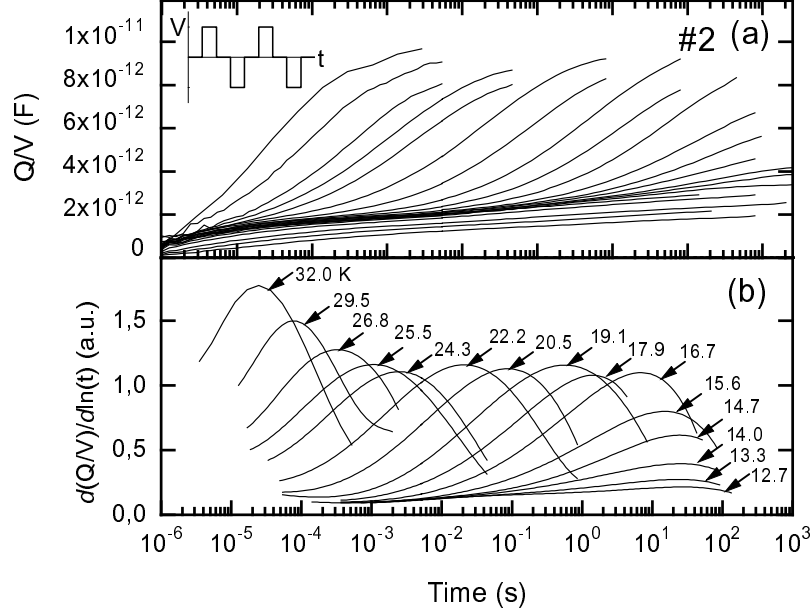


FIG. 1. (a) Typical real-time relaxation of the polarisation charge curve set of o-TaS₃ crystal (#2) in the linear response region. (b) Respective set of the logarithmic derivatives for the same sample.

on different t_p , like it was observed recently in K_{0.3}MoO₃ [16]. It has been checked up that the results reported here are not affected by this observed dependence and correspond to the infinite duration of the polarisation pulse.

Fig. 1(a) demonstrates a typical set of $Q(t)$ curves for pure and doped TaS₃ samples. The relaxation of the polarisation is nonexponential; it continues to the longest times at which measurements were carried out.

For all samples at temperatures above approximately $T = 10$ K we have observe a region with a comparatively rapid growth of $Q(t)$ with time. This relaxation mode gives a sharp maximum on a logarithmic derivative $dQ/d \log t$ of the polarisation (Fig. 1(b)) indicating passing of the temperature-dependent characteristic time; in agreement with earlier studies [2–6,14].

Fig. 1(b) shows the respective set of the logarithmic derivative of the relaxation curves, $d(Q/V)/d \log t$. The characteristic time, τ , is determined as a time corresponding to the maximum of the derivatives.

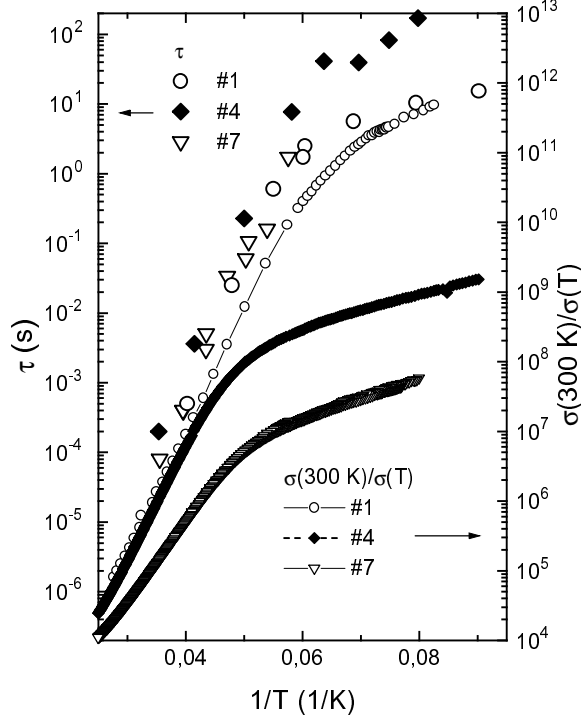


FIG. 2. Temperature-dependent characteristic time found from the real-time relaxation data together with the linear conduction data.

Fig. 2 shows typical temperature dependencies of the characteristic time τ of a pure and two doped samples. The high-temperature part of $\tau(1/T)$ dependence ($T \geq T^* \simeq 17$ K) can be fitted by the activation law with the activation energies 440 ± 40 K. The values of the crossover temperature T^* , as well as the activation energies E_ε , are remarkably nearly the same for all samples (within 10% experimental error), i.e. they are independent of a crystal purity (see Table I). Moreover, the relaxation time at a fixed temperature does not correlate to neither type nor nominal concentration of the impurities in the studied samples. For example, doping by Nb increases $\tau(20$ K) from 8×10^{-2} s (sample 3) to 2×10^{-1} s (sample 4) and 5×10^{-1} s (sample 5), whereas doping by Ni decreases it down to 2×10^{-2} s (sample 6) with respect to the most pure crystals 1-3.

We also observed another branch of $\tau(1/T)$ dependence. Note that the heights of maximums of $d(Q/V)/d \log t$ curves (Fig. 1(b)) are approximately the same at $25 \geq T \geq T^*$ K, but decrease rapidly at $T < T^*$ K. Similarly, the slope of $\log \tau$ vs. $1/T$ curve at $T < T^*$

is roughly by factor 4 lower than at $T > T^*$. This indicates that there is a change of the relaxation mechanisms around T^* . Suggesting the activation law for the low-temperature part of $\tau(T)$ one gets the estimate for the activation energy around 120 ± 50 K depending on doping impurity.

In addition, measurements of the DC linear conduction temperature variation $\sigma(T)$ were carried out for the same samples for the temperature range $T < 50$ K. Fragments of $\log(1/\sigma(T))$ vs. $1/T$ curves are shown in Fig. 2. A region of the activation dependence, $\sigma \propto \exp(-E_\sigma/T)$, is observed above 20 K, in agreement with the results of earlier studies. Note that while the slopes of $\log(\tau(1/T))$ curves are very close to each other, the slopes of $\log(\sigma(1/T))$ curves are different. The respective set of E_σ demonstrates their distinction from E_ϵ (See Table I).

Direct measurements of the dielectric constant has shown that ϵ of impure crystals is higher than of pure ones (see Table I). To verify this result we also measured the ratio $\sigma''(f, 10 \text{ K})/\sigma(100 \text{ K})$ (σ'' is an imaginary part of the AC conduction) which is independent of the geometrical factors. As $\sigma(100 \text{ K})$, is practically independent of impurity concentration, this ratio can be considered as a measure of the low-temperature dielectric constant. And again, it was found that $\sigma''(1 \text{ kHz}, 10 \text{ K})/\sigma(100 \text{ K})$ is higher for impure crystals than for pure ones. That reflects growth of the low-temperature ϵ with increase of impurity concentration. Note that this unusual low-temperature behaviour of $\epsilon(n_i)$ is opposite to the high-temperature behaviour corresponding to the relation $\epsilon \propto 1/E_T$ well-known for the high-temperature region [17].

IV. DISCUSSION

As was noted above, absence of any correlation between the characteristic time and impurity content does not support the earlier suggestion [5,6] on the disorder-induced glass transition as a mechanism responsible for the low-temperature dielectric anomaly.

In principle, the strong-pinning model [8] may provide impurity independent activation

energy for the relaxation time. Namely, in the original model [8] the depinning barrier height depends on the pinning potential and may be arbitrary large. One should expect, however, that when the pinning potential exceeds some critical value, a new alternative channel for depinning of the CDW appears. For example, depinning of the CDW may occur through a suppression of the order parameter and local phase slip, rather than through further shift of the continuous CDW. The respective energy barrier depends mostly on parameters of the CDW itself rather than on its interaction with impurity. Nevertheless, the strong-pinning model [8] predicts qualitatively different dependencies of the dielectric constant on the impurity concentration than it was observed. Namely, it gives $\epsilon^{-1} = \epsilon_w^{-1} + \epsilon_s^{-1}$, where ϵ_w and ϵ_s are the weak and strong-pinning components respectively. At $T < T^*$ both components are expected to *decrease* with growing impurity concentration [8], the value of ϵ should be lower for doped crystals. In contrast, our experimental data clearly indicate growth of ϵ with increasing n_i (see Table I). So the strong-pinning model [8] is inconsistent with the data.

As was noted above, the screening model [7] is consistent with the high-temperature dielectric anomaly observed in $\text{K}_{0.3}\text{MoO}_3$ [2–4], $(\text{TaSe}_4)_2\text{I}$ [10] and TaS_3 [11,12] at $T \sim T_P/3$, where CDW deformations are screened by normal carriers excited over the Peierls gap. To apply similar explanation to the low-temperature anomaly in TaS_3 one needs to suggest existence of screening carriers with the activation energy around 400 K [18]. However, the present version of the screening theory [7] can hardly account for the opposite relations between ϵ and n_i for high- (decrease of ϵ with n_i) and low-temperature ranges (increase of ϵ with n_i).

So neither of available explanations of the low-temperature dielectric anomaly of TaS_3 is consistent with the actual dependencies of $\epsilon(n_i)$ and $\tau(T, n_i)$. The most surprising result is growth of the dielectric constant with increase of impurity concentration (see Table I). Note, such a behaviour may reflect the decrease of the pinning energy W_p per the phase-correlation volume with growth of n_i : in the weak-pinning case $W_p \propto 1/n_i$ (see e.g. Ref. [19] and references therein). Thus growths of both the low-temperature linear DC conduction observed

earlier [20] and AC conduction reported here with increase of the impurity concentration are consistent with general expectations for creeping of weakly pinned CDW. Additional contribution to ϵ may also come from increase of CDW dislocation density with increase of n_i [21].

Another surprising result is independence of E_ϵ on impurity type and concentration. This result indicates the existence of low-energy excitations in TaS₃ that mediate the relaxation process. Though possible contribution of such excitations into low-temperature transport properties of TaS₃ was broadly discussed earlier [18], no their contribution into the low-temperature conduction was observed in the present measurements.

In conclusion, the characteristic time of low-temperature polarisation of TaS₃ is found to follow the activation law with the activation energy ~ 400 K independent of the dominant impurity and its concentration. In addition, the low-temperature dielectric constant of doped samples is found to be higher than of pure ones. The observed behaviour is inconsistent with all earlier suggested explanations of the low-temperature dielectric anomaly and implies existence of low-energy excitations having the activation energy 400 K and mediating the polarisation process.

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exponentially with lowering temperature. So one can expect that at sufficiently low
temperatures nucleation of CDW dislocations reducing the CDW strain is energetically
favourable. As a result, the CDW gets additional degree of freedom and may be more
polarisable than a rigid CDW without dislocations.